Overview and Synthesis of High-Nickel Nickel Manganese Cobalt Oxide (NMC) Cathodes

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The University of Texas at Austin

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OVERVIEW

Timeline

- Project start date: October 2016
- Project end date: September 2021
- 30 % complete

Budget

- Total project funding
  - DOE: $50,000K
- Funding received in FY 2017
  - $ 10,000 K
- Funding for FY 2018
  - $ 10,000K

Barriers

- Barriers
  - Cycle and calendar life
  - Thermal-abuse tolerance
  - Air sensitivity
- Targets
  - High-energy-density high-nickel NMC cathodes with long service life and acceptable thermal stability

Partners

- PNNL, SLAC, INL, BNL, UW, UCSD, BU

RELEVANCE

Overall Project Objective

- Develop high-energy, long-life, safe high-nickel NMC cathodes
  - High-nickel NMC cathodes with a specific capacity of 200 – 250 mA h g^{-1}
  - Stabilization strategies for long cycle and calendar life
  - Stabilization strategies for acceptable thermal stability

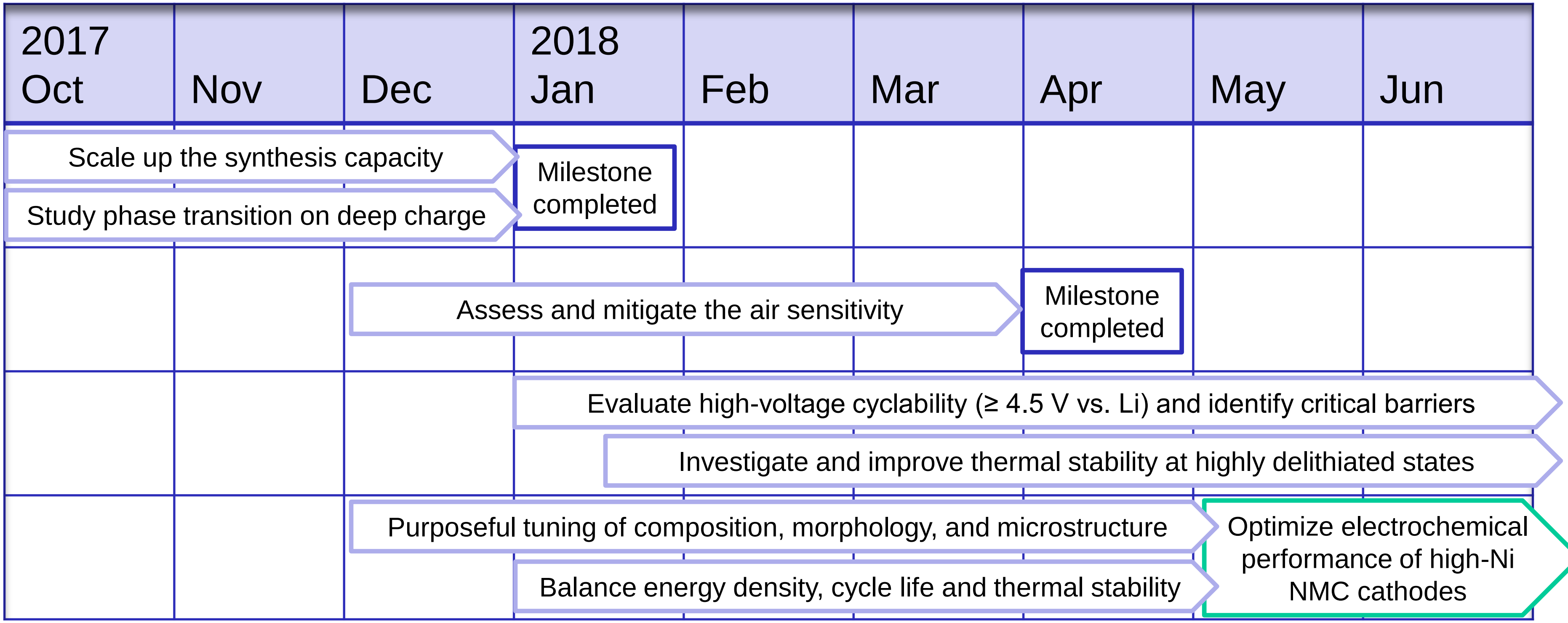
Objectives for Year 2

- Synthesis scale-up and optimization of high-Ni NMC with in-depth investigation of their structure-morphology-property relationships
  - Scale up synthesis capacity with a careful control
  - Understand and suppress bulk and surface degradation during cycling
  - Assess and mitigate air sensitivity with compositional and surface control
  - Evaluate high-voltage cyclability and identify critical barriers
  - Balance energy density, cycle life, and thermal stability
  - Optimize electrochemical performance

MILESTONES

Month/Year	Milestone	Status
December 2017	Technical: (i) Scale up the synthesis capacity of high-Ni NMC to 500 g, and (ii) assessment of the structural and phase evolution as a function of depth of charge-discharge for high-Ni cathodes with various Ni contents	Completed
March 2018	Technical: Evaluation of the degree of reaction with ambient air of the high-Ni cathodes with various Ni contents	Completed
June 2018	Technical: Assessment of the cutoff charge voltages on the long-term cyclability of high-Ni cathodes with various Ni contents	Ongoing
September 2018	Technical: Evaluation of the thermal stability of high-Ni cathodes with various Ni contents at delithiated states	Ongoing

APPROACH



- **Milestones for Year 2 (FY 2018)**
  - The Milestones on the scale-up synthesis and preliminary structural/chemical evaluation of high-Ni NMC cathodes have been completed (marked as *Milestone completed* above)

TECHNICAL ACCOMPLISHMENTS AND PROGRESS

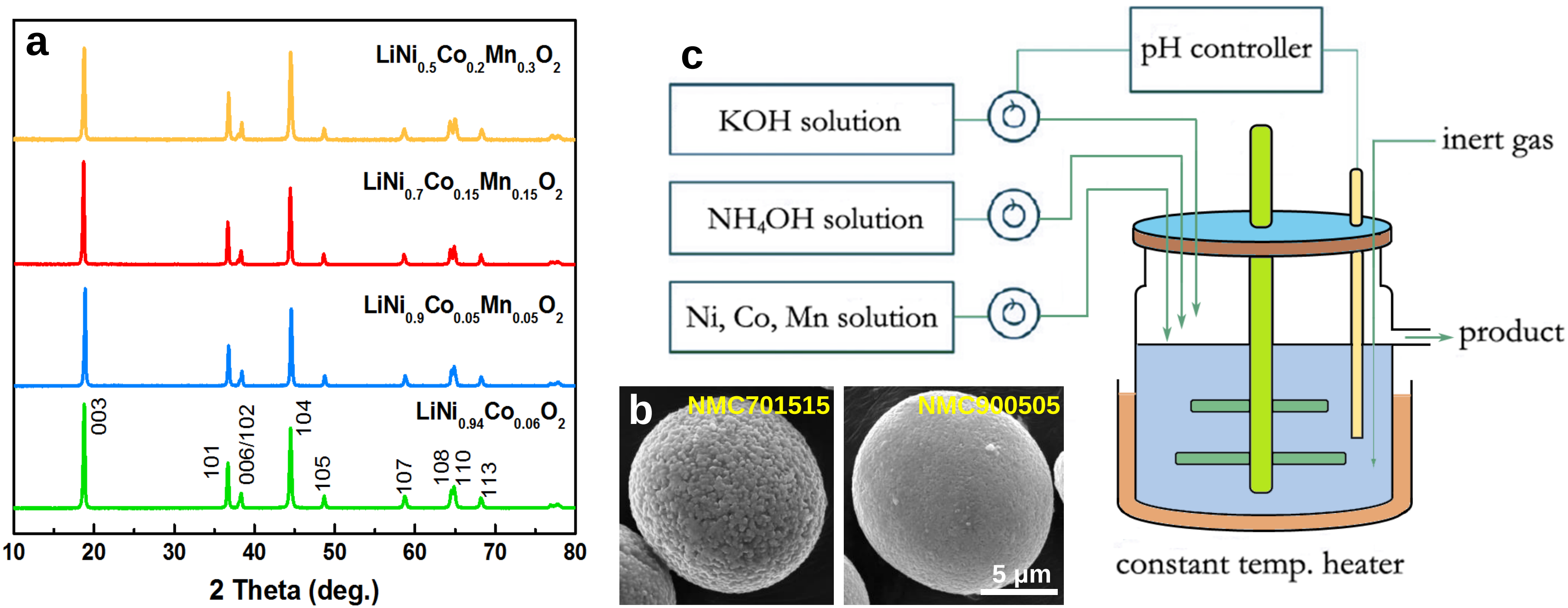
- (Y1Q1 – Y1Q4) The material chemistry database developed provides a guideline for (i) essential synthetic parameters for successful scaling up of the transition-metal co-precipitation of high-Ni NMC cathodes, and (ii) purposeful design of high-nickel NMC with balanced performance metrics (energy density, cycle life, thermal stability, *etc.*)

- (Y2Q1) Scaled up synthesis of high-nickel NMC cathodes (> 1.5 kg product yield per batch) with good electrochemical properties comparable or superior to commercial samples; revealed and suppressed the structural degradation of high-nickel NMC at highly delithiated states through proper cation doping (*e.g*., Al)

- (Y2Q2) Assessed and suppressed air sensitivity of high-Ni NMC:
  - (i) correlation between air sensitivity and nickel contents
  - (ii) degradation mechanism in ambient environment demonstrated
  - (iii) drastically inhibited air reactivity of high-Ni cathodes by Al^{3+} doping (~ 80% reduction in capacity deterioration after 30-day storage)

SCALE-UP SYNTHESISS OF HIGH-NICKEL NMC

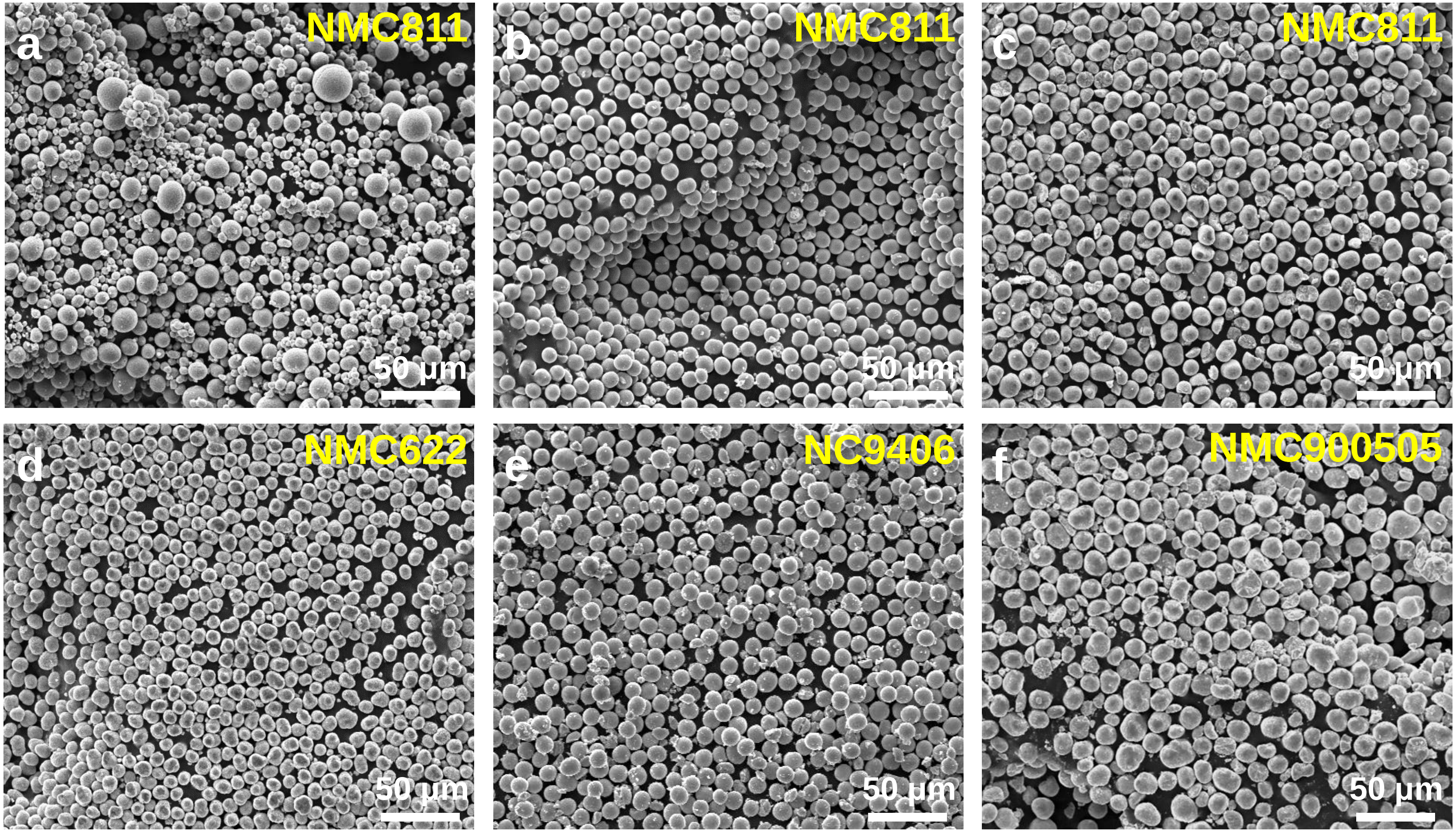
- Compositions: $LiNi_{1-x-y}Co_xMn_yO_2$ (Ni contents of 0.3 – 0.94)
- Careful control of temperature, pH, pumping rate, etc.



Synthesis of high-Ni cathodes: (a) XRD and (b) SEM of selected samples, and (c) diagram of co-precipitation

- (Y1Q1 – Y1Q4) A series of high-Ni cathodes with varying Ni contents have been prepared through co-precipitation with relatively small yield per batch (200 – 500 g)
- (Y1Q4 – Y2Q1) Hydroxide precursors have been scaled up to > 1.5 kg per batch

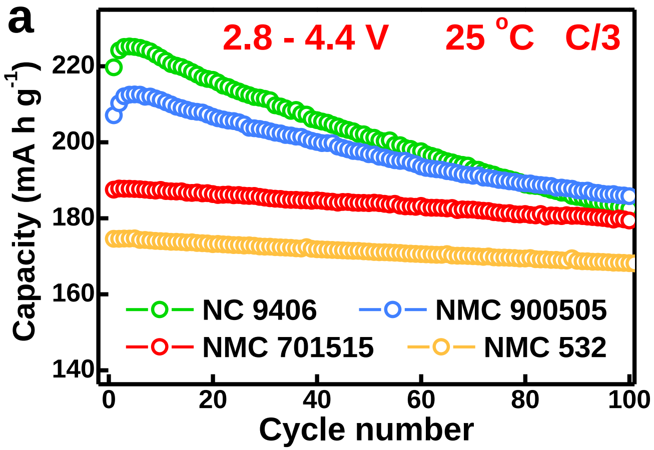
MORPHOLOGY OF SYNTHESIZED HIGH-NICKEL NMC



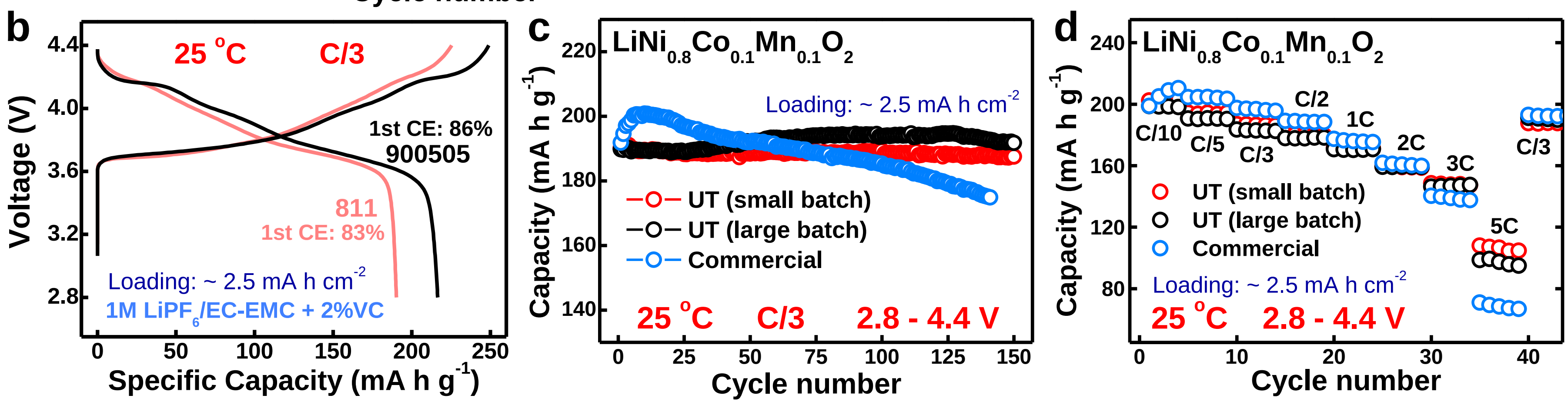
SEM images of high-Ni cathodes: (a), (d) commercial, (b), (e) UT (200 – 500 g yield) and (c), (f) UT (> 1.5 kg yield)

- The scaled up high-Ni NMC shows consistent particle morphology with small-batch samples prepared previously, which is also similar to commercial samples (NMC622)

ELECTROCHEMICAL PERFORMANCE OF HIGH-NICKEL NMC



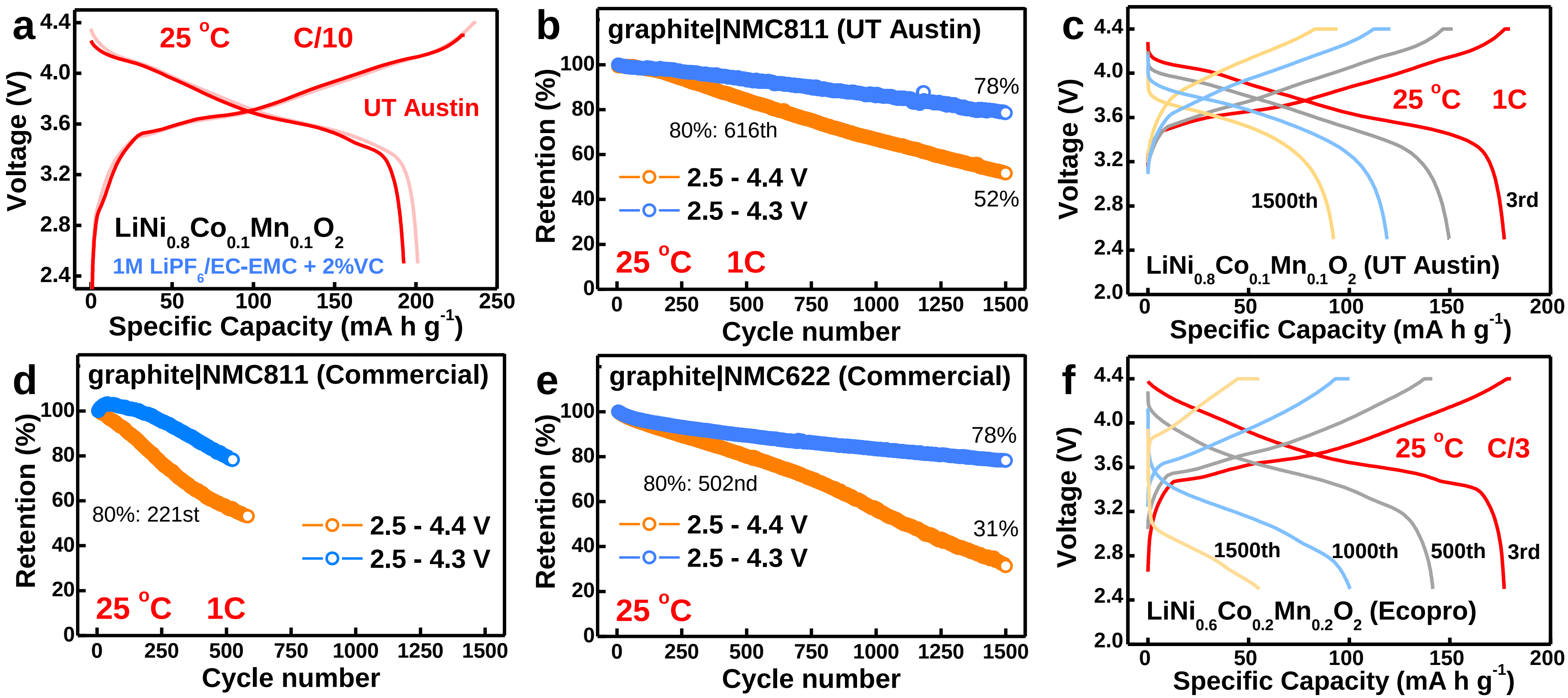
- Benefits with high-Ni NMC:
  - High energy density
  - Superior kinetic response
- Issues with high-Ni NMC:
  - air sensitivity
  - limited electrochemical durability
  - low thermal-abuse tolerance



Cell performance of high-Ni cathodes: (a) cycling (multiple small-batch samples), (b) initial voltage profiles (large-batch 811 and 900505), and (c) cyclability, (d) rate performance (small-/large-batch and commercial 811)

- (Y1Q4 – Y2Q2) Large-batch NMC 811/900505 demonstrate good electrochemical properties, comparable to commercial NMC811 (further optimization still underway)

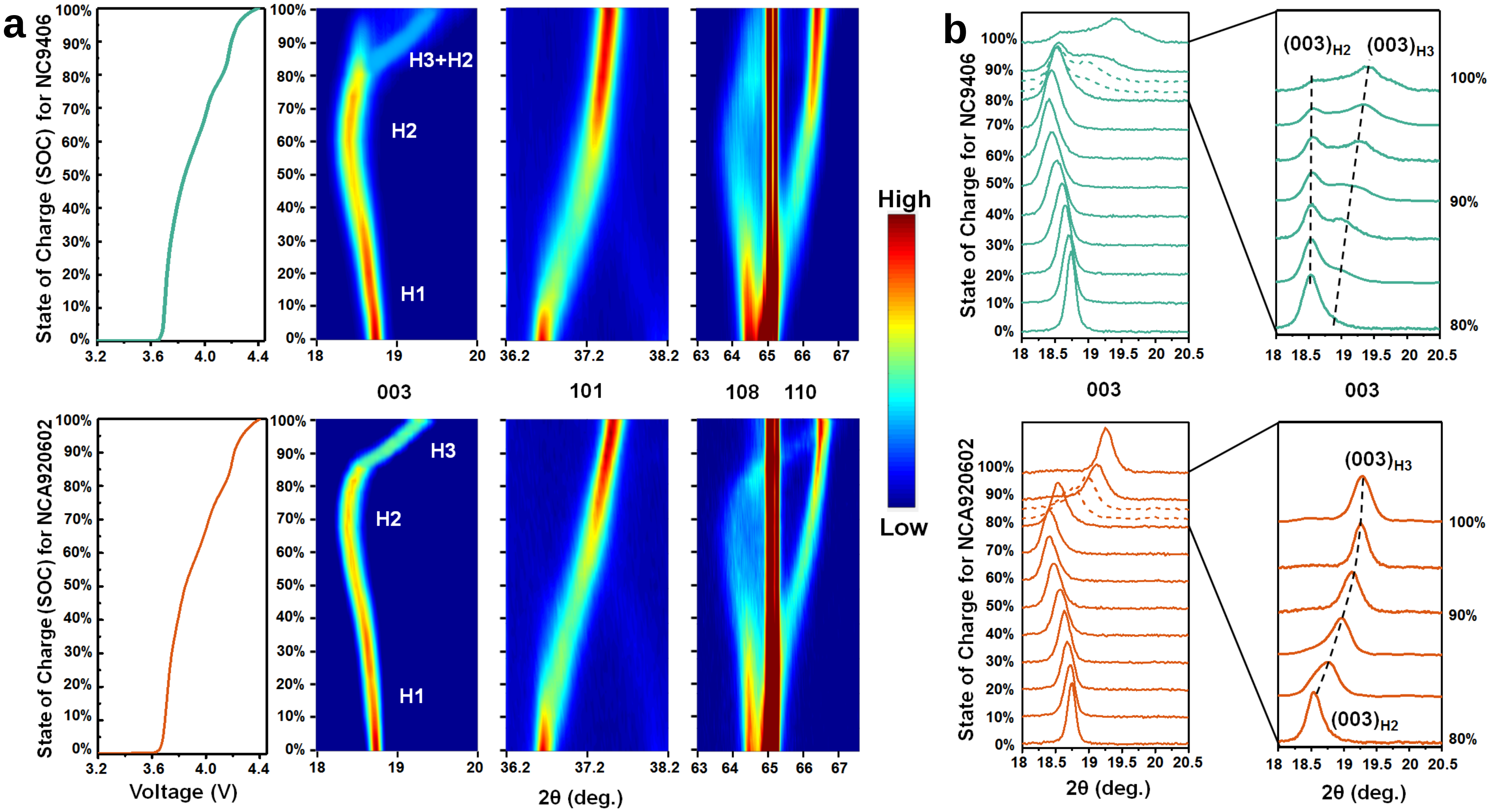
SCALE-UP SYNTHESISS OF HIGH-NICKEL NMC



Long-term cyclability of high-Ni NMC: (a) initial voltage profiles of 811 (UT), cycling stability of (b) 811 (UT), (d) 811 (commercial), and 622 (commercial), and evolution of voltage profiles of (c) 811 (UT) and 622 (commercial)

- (Y1Q2 – Y2Q2) To evaluate the long-term cyclability of high-Ni cathodes, pouch-type full cells with graphite anode were assembled, which enable stable cycling of > 1,500 cycles
- NMC811 (UT-Austin) outperforms even NMC622 (commercial) in long-term cyclability, and is substantially more stable than NMC811 (commercial) based on preliminary data

STRUCTURAL EVOLUTION OF HIGH-NICKEL NMC ON CHARGE

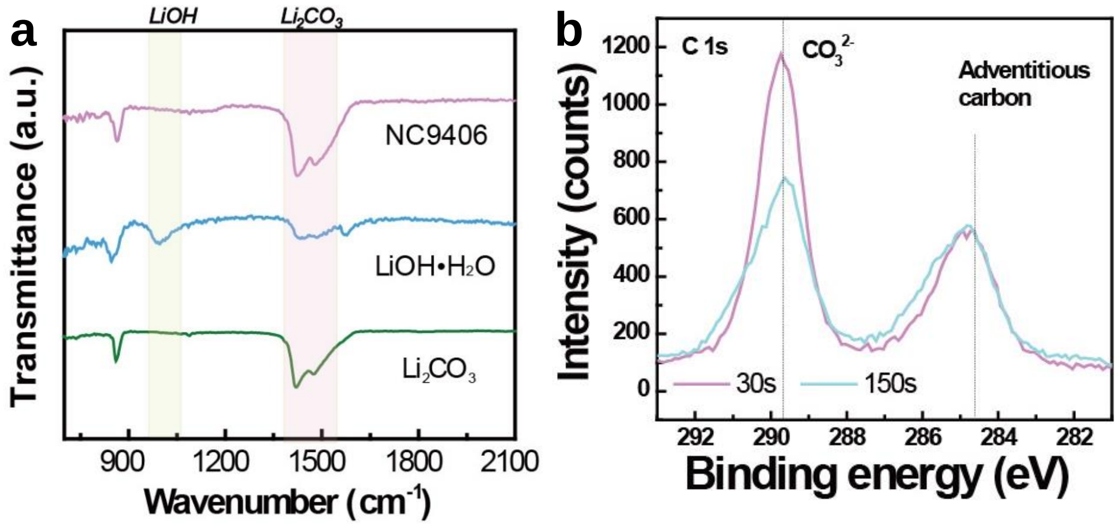


In-situ XRD of NC9406 and NCA920602 during first charge: (a) contour plot of the diffraction patterns of the (003), (101), (108), and (110) peaks, and (b) detailed XRD patterns of the (003) peak at different SOC

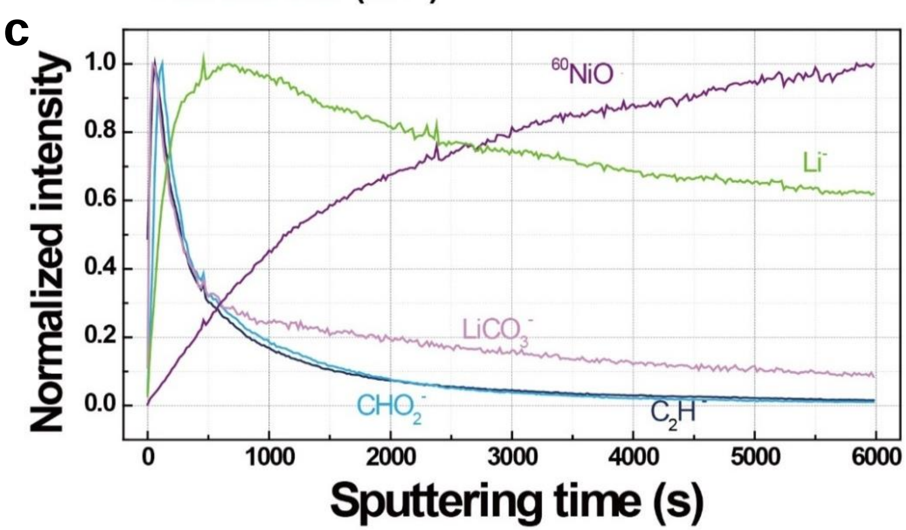
- (Y2Q1) Al-doping in NC9406 tunes the H2/H3 phase transition and reduces lattice strain

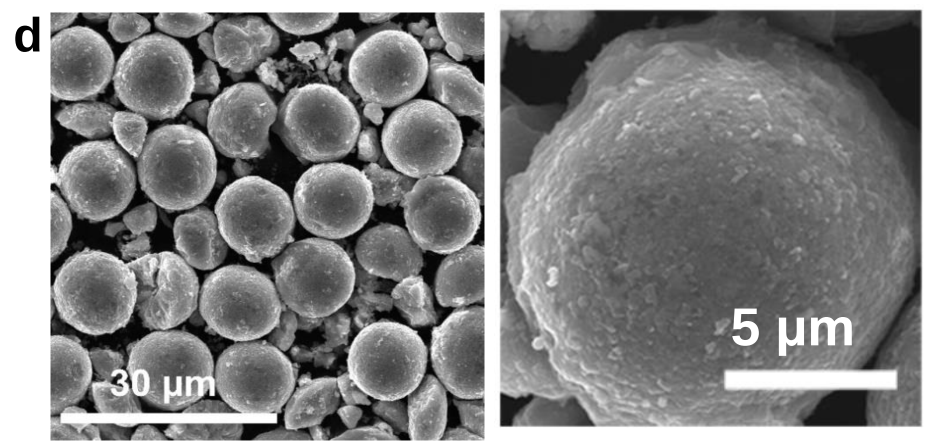
J. Li, W. Li, S. Wang, K. Jarvis, J. Yang, A. Manthiram, (submitted)

AIR SENSITIVITY OF HIGH-NICKEL NMC



- (Y2Q2) Surface-sensitive characterization tools are used to probe the degradation of high-Ni cathodes (NC9406) in ambient environment
- The degradation products, including residual lithium species and adsorbed species (carbonates) appear localized on the surface

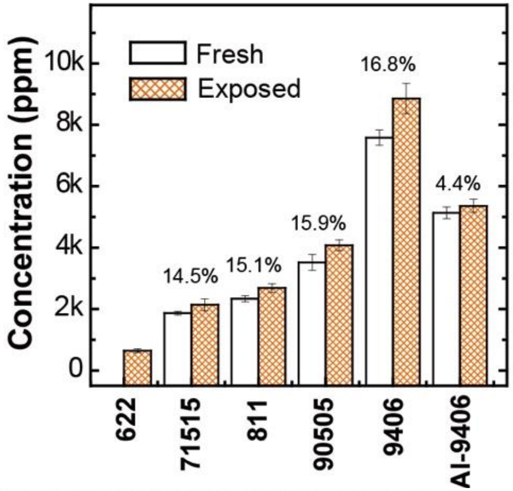


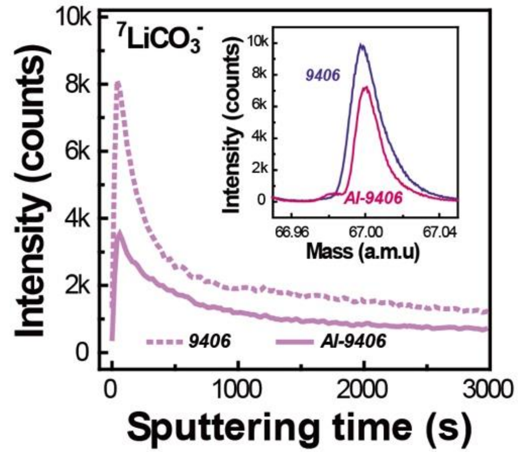


Degradation products formed on NC9406 in ambient environment: (a) FTIR, (b) XPS C1s, (c) TOF-SIMS, and (d) SEM

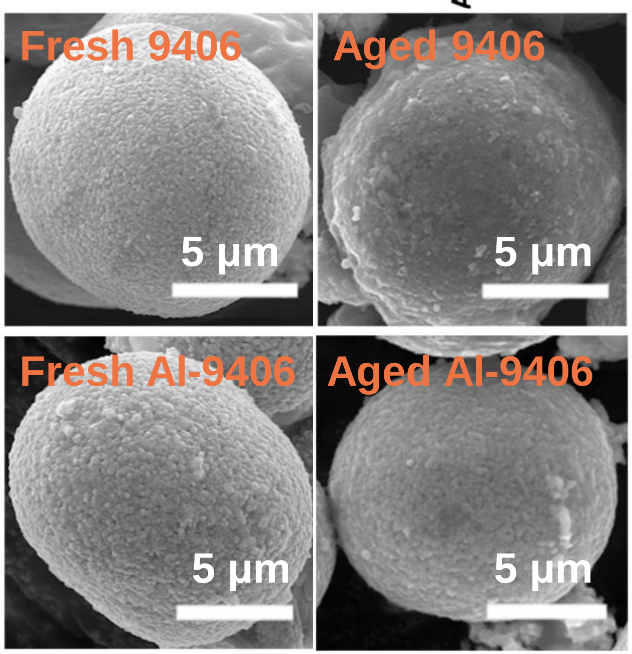
Y. You, H. Celio, A. Dolocan, J. Li, A. Manthiram, *Angewandte Chemie International Edition* (in press)

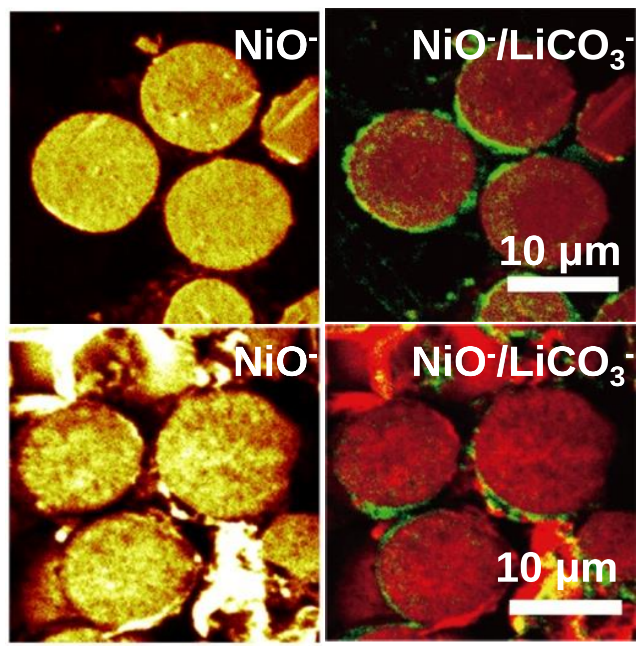
IMPROVING THE AIR STABILITY OF HIGH-NICKEL NMC





Samples	Atomic ratio of CO_3^{2-}/Ni
Fresh 9406	1.8
Aged 9406	54.6
Fresh Al-9406	1.7
Aged Al-9406	28.4

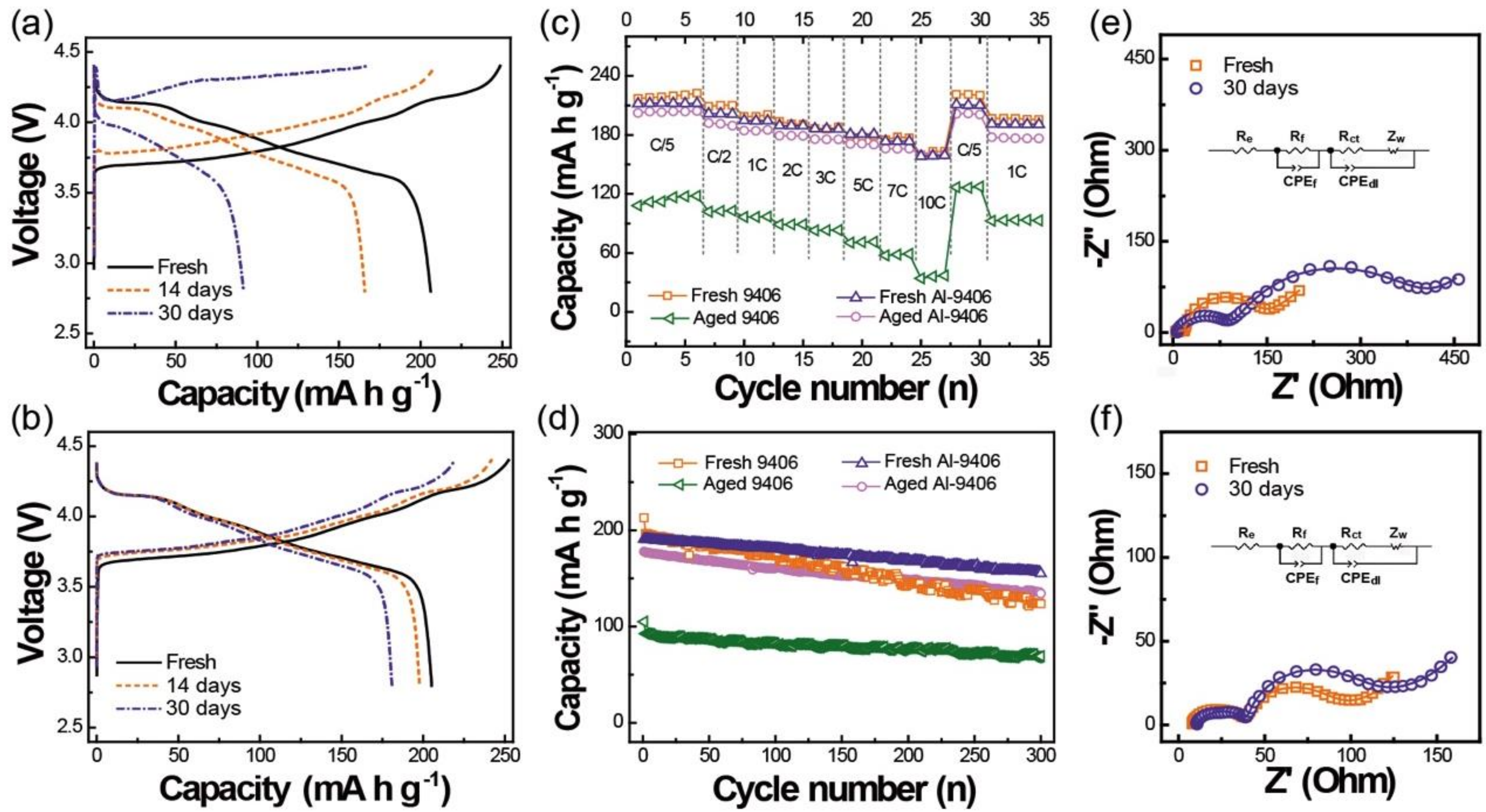




- Higher nickel content leads to higher amounts of residual Li and lower air storage stability
- Al doping effectively suppresses the air sensitivity issue of NC9406

Y. You, H. Celio, A. Dolocan, J. Li, A. Manthiram, *Angewandte Chemie International Edition* (in press).

IMPROVING THE AIR STABILITY OF HIGH-NICKEL NMC

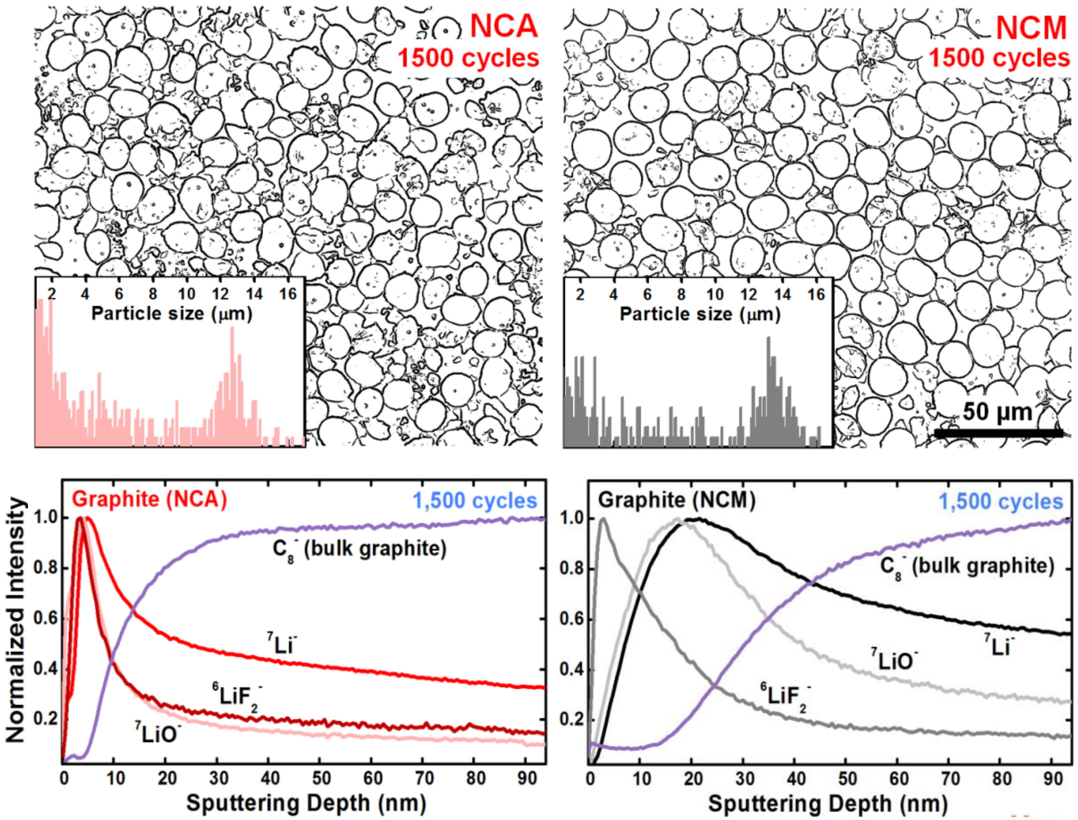


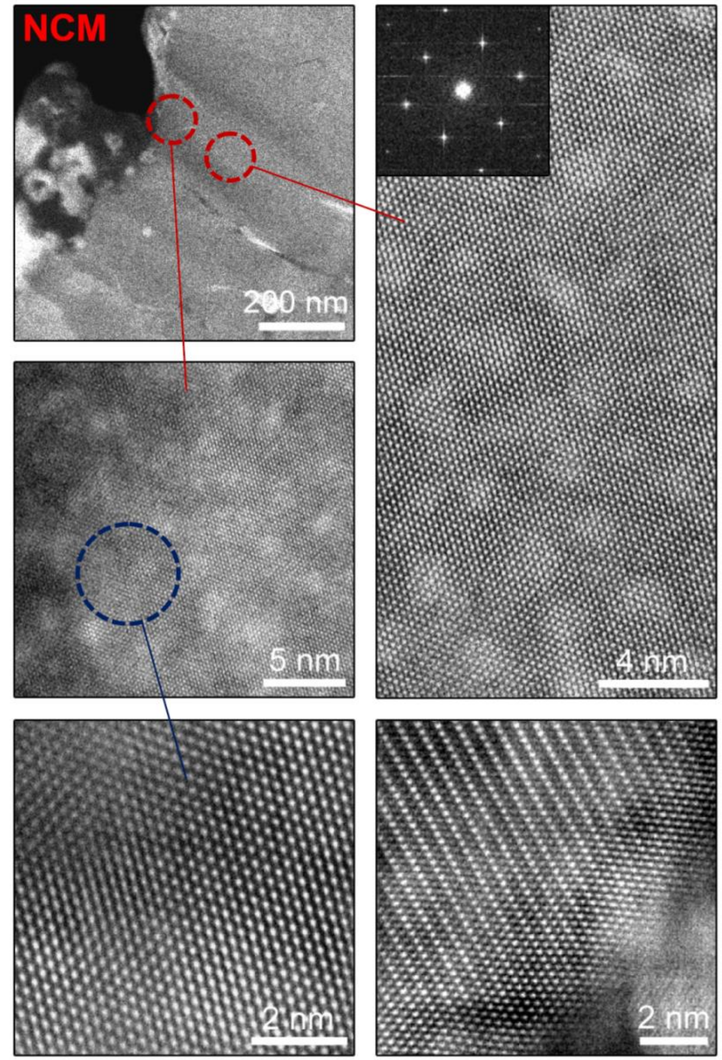
Electrochemical performance of (a), (c), (e) NC9406 and (b), (d), (f) NCA920602 before and after air exposure

- (Y2Q2) Al-doped NCA920602 retains the electrochemical performance (capacity, rate capability, and cyclability) much more than NC9406 after air exposure for 30 days, which are also supported by the mitigated impedance increase

Y. You, H. Celio, A. Dolocan, J. Li, A. Manthiram, *Angewandte Chemie International Edition* (in press)

$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) vs. $LiNi_{0.7}Co_{0.15}Mn_{0.15}O_2$ (NMC)





- NCA suffers from more secondary particle cracking
- NMC701515 suffers from more transition-metal dissolution (esp. Mn) and crossover to graphite
- NMC701515 suffers from more surface irreversible layered-to-rock-salt phase transition

W. Li, X. Liu, H. Celio, P. Smith, A. Dolocan, M. Chi, and A. Manthiram, *Advanced Energy Materials*, **2018**, 8, 20173154

RESPONSE TO REVIEWERS' COMMENTS

No presentation was given in the previous year

COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

- Jie Xiao, Pacific Northwest National Laboratory

  Electrochemical evaluation of high-nickel NMC paired with Li-metal anode

- Peter Khalifah and Xiao-Qing Yang, Brookhaven National Laboratory

  Structural characterization of a series of high-nickel NMCs

  - Synchrotron X-ray scattering
  - Neutron scattering
  - Effect of post annealing

- Ping Liu, University of California at San Diego

  Preliminary electrochemical evaluation of large-batch NMC811 and the effect of secondary particle size on electrode architecture (NMC701515)

- Jihui Yang, University of Washington at Seattle

  Structural characterization of high-Ni cathodes with *in-situ* X-ray scattering

REMAINING CHALLENGES AND BARRIERS

- **Challenge/Barrier 1:** In spite of excellent long-term cyclability, NMC811 prepared at UT-Austin delivers slightly lower specific capacities compared to commercial 811. In addition, with scaled up synthesis, we notice a small fraction of secondary particles appear fragmented in as-prepared samples. Therefore, we will continue to tune and optimize our transition-metal co-precipitation routine.

- **Challenge/Barrier 2:** There exists a trade-off relationship among the high-Ni NMC family in terms of energy density, cyclability, and thermal stability. With the current push to higher Ni contents in NMC cathodes, cycle/calendar life (especially at elevated temperatures) and thermal-abuse tolerance need to be improved for practical applications. Thus, we will apply a variety of surface/bulk stabilization strategies to address this challenge.

PROPOSED FUTURE WORK

- FY2018
  - To address Challenge/Barrier 1: We have developed extensive experiences in the transition-metal co-precipitation synthesis with relatively small yield (< 500 g per batch). A careful control/tuning of the reaction temperature, pH, precursor feeding rate, stirring rate, and total time will be applied to optimize the overall quality of the final product.
  - To address Challenge/Barrier 2: After optimization of the scaled up high-Ni cathodes (> 1.5 kg per batch), a series of surface/bulk stabilization strategies (coating/doping and electrolyte modification) will be applied to enhance their cyclability and thermal stability.
  - (Q3 July-18) Technical Milestone III: We are assessing the long-term cyclability of NMC811 in pouch-type full cells with various charge voltage cutoffs (4.2 – 4.5 V) over 1,500 cycles, and will apply a diversity of characterization techniques to identify critical barriers limiting the high-voltage cyclability of high-Ni cathodes.
  - (Q4 Sep-18) Technical Milestone IV: We will use DSC to systematically investigate the poor thermal-abuse tolerance of high-Ni cathodes at highly delithiated states, and explore strategies, such as elemental doping and electrolyte modification, to address the problem.
- FY2019
  - (Q1 Dec-19) Technical Milestone I: We will focus on the lithiation treatment of high-Ni NMC in large amounts, following the scaled up co-precipitation process. The effect of excess Li source, oxygen flow rate, cooling/heating rate, total heating time, *etc*. will be studied, and the knowledge gained can further enhance the properties of the final product.

SUMMARY

- The material chemistry database and characterization methodology developed are facilitating the selection of desired high-Ni NMC cathode candidates with balanced performance metrics (Y1)
- The scaled-up high-Ni cathodes achieve the following (Y1Q4 – Y2Q1):
  (i) tap density (~ 2.5 g cm^{-3}) comparable to commercial samples
  (ii) capacities (190 – 220 mA h g^{-1}) comparable to commercial samples
  (iii) excellent long-term cyclability (> 80% retention after 1,000 cycles)
- Assessment of the structural evolution demonstrates that (Y2Q1): High-Ni cathodes exhibit complex phase transitions detrimental to cycling performance, which can be suppressed with proper elemental doping
- Evaluation of the air sensitivity of high-Ni cathodes reveals that (Y2Q2):
  (i) the degradation mechanism of high-Ni NMC cathodes in air
  (ii) the air sensitivity can be suppressed with proper elemental doping